Partitioning of elements in a entrained flow IGCC plant: Influence of selected operational conditions

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A B S T R A C T

The partitioning of trace elements and the influence of the feed conditions (50:50 coal/pet-coke feed blend and limestone addition) was investigated in this study. To this end feed fuel, fly ash and slag samples were collected under different operational conditions at the 335 MW Puertollano IGCC power plant (Spain) and subsequently analysed. The partitioning of elements in this IGCC plant may be summarised as follows: (a) high volatile elements (70–>99% in gas phase): Hg, Br, I, Cl and S; (b) moderately volatile elements (up to 40% in gas phase and ⩾60% in fly ash): As, Sb, Se, B, F, Cd, Tl, Zn and Sn; (c) elements with high condensation potential: (>90% in fly ash): Pb, Ge, Ga and Bi; (d) elements enriched similarly in fly ash and slag 30–60% in fly ash: Cu, W, (P), Mo, Ni and Na; and (e) low volatile elements (>70% in slag): Cs, Rb, Co, K, Cr, V, Nb, Be, Hf, Ta, Fe, U, Ti, Al, Si, Y, Sr, Th, Zr, Mg, Ba, Mn, REEs, Ca and Li. The volatility of As, Sb, and Tl and the slagging of S, B, Cl, Cd and low volatile elements are highly influenced by the fuel geochemistry and limestone dosages, respectively.

1. Introduction

Studies on the partitioning of trace elements in commercial IGCC plants are scarce [1–4] and most of them based on experiments carried out at laboratory and pilot plant scale [5–9], and on modelling of the gas phase [10,11].

The implementation of IGCC plants at industrial scale is expected to growth in the forthcoming years. Among the three most common types of gasification technologies (entrained flow, fixed bed and fluidized bed) the entrained flow gasification systems have been the choice of industry for current IGCC systems [12]. These three types of gasification technologies differ in a number of operational conditions including feed system of coal, the temperature and pressure and the coal size input [12], the highest gasification temperature (1200–1600 °C) and pressure (25–40 bar) and the lowest feed coal size (0.1 mm) being attained in entrained flow gasifiers. The fixed bed gasifier is characterised by having the largest size of feed coal (3–30 mm) and the lowest temperatures (400–1150 °C), with a wide range of pressure (10–100 bar), while fluidized bed gasifiers reach intermediate temperatures (800–1050 °C), pressures (10–25 bar) and feed coal sizes (1–5 mm). Furthermore, these gasification technologies have different ash removal systems and temperature. The different operational parameters showed above may result in a different behaviour and fate of elements depending on the gasification technology applied. Consequently, studies on the fate of trace elements in gasification systems are thus being necessary to progress on trace pollutants abatement in IGCC plants.

In pulverised coal combustion (PCC) plants trace elements are partitioned among the slag/bottom ash, fly ash or flue gas according to their volatile behaviour, their mode of occurrence in coal and the operational parameters of the PCC plants [13–20]. The classification of elements proposed by Meij [14] has been commonly used as a reference for subsequent partitioning studies. This classification is based on the enrichment factors (EFs) of the elements in bottom ash and fly ash during coal combustion classified in three groups: Class I includes the non-volatile elements (Al, Ca, Cs, Fe, Hf, Mg, Sc, Si, Sr, Th, Ti and REEs); Class II comprises the volatile elements condensing on ash particles. These elements are in increasing condensation potential or enrichment factor (EF) in fly ash: Ba, Cr, Mn, Na and Rb (Class IIc); Be, Co, Cu, Ni, U, V and W (Class IIb), and As, Cd, Ge, Mo, Pb, Sb, Tl and Zn (Class IIa). The Class III comprises the highly volatile elements (B, Br, C, Cl, F, Hg, I, N, S and Se), which remain totally or partially in gas phase at fly ash removal temperatures.

As stated above due the relatively new and scarce implementation of IGCC at commercial scale, few studies on the partitioning of elements have been elaborated. Studies on partitioning of elements in fixed bed gasifiers [2–4] have revealed a similar behaviour of a number of elements in coal combustion. These studies reported Hg as highly volatile element and Se, Cd, Pb, As (in decreasing order) as volatile elements during gasification with subsequent condensation on ash particles. Copper, Mo, Ni and Zn showed a relatively low volatilisation and condensation while Ba, Co, Cr, Mn and V were found as non-volatile elements. The first studies on partitioning of elements in entrained flow gasifiers [8] were based on combining experimental data and thermodynamic equilibrium calculations, and reported a significant volatile fraction of As, Se, Sb, Pb and Hg (remaining in the vapour phase at 500–600 °C), while Cd, Cr, Co, Mn, Ni, U and Th are relatively non-volatile. Other studies on this topic [10], reported the formation of Fe–Mn sulphide and Na–K chloride species at the highest cooling temperatures (900 and 800 °C, respectively) and subsequent condensation of Zn, Pb and As sulphide species at temperature ranges of 810–220, 520 and 380 °C, respectively. The modelling studies carried by Diaz-Somoano and Martinez-Tarazona [11] for a number of trace elements in entrained flow gasifiers, at different gas atmospheres and pressures and at subsequent cooling temperatures, predicted relatively high volatile fractions of Sb, As, Cd, Pb, Zn and Ni at high Cl gasification atmosphere and high condensation of these elements (mainly as sulphide species) at low Cl and high H_2S gasification atmospheres and at fly ash removal temperatures between 200 and 300 °C.

Despite the restrictions of the thermodynamic calculations, the above predicted behaviour, speciation and condensation temperatures for a number of elements in entrained flow gasifiers are in relatively accordance with those obtained from samples deposited on the cooling system of the commercial scale Puertollano IGCC power plant [21,22]. Studies in this plant have revealed the formation of Fe–Ni–V sulphide species segregated on the fly ash particles at high temperatures (~1200 °C), partially reacting with gaseous As and Sb to form Fe–Ni arsenide–antimonide species at 800 °C and the subsequent condensation of gaseous sulphide species, with the prevalence of galena (PbS) at 520–750 °C, sphalerite (ZnS) and Ge species at 520–470 °C and wurtzite (ZnS) at 300–400 °C.

In this study the partitioning of elements during the gasification is evaluated for a number of solid streams representative of different feed fuel characteristics and operational conditions in the Puertollano IGCC plant. This plant is fed with a mixture of a local high volatile bituminous coal rich in metals and semi-metals [23] and pet-coke, supplied by a nearby oil refinery. Limestone is added (2–4%) to the feed fuel blend as a fluxing agent. The gasification is carried out in a pressurised entrained flow gasifier working under slagging conditions and at 1200–1600 °C and 25 bars. The influence of a number of operational conditions (the slag/fly ash ratio, the flue gas cooling, co-gasification of coal and pet-coke and the addition of limestone as a fluxing agent) on the partitioning of the elements among the IGCC by-products and flue gas is evaluated.

2. Materials and methods

For the study of the partitioning of trace elements among flue gas, slag and fly ash, four set of samples were selected from the operational period 2001–2005 of the Puertollano IGCC plant. Each sample set containing simultaneously collected samples of coal, pet-coke, limestone, feed fuel blend, slag and fly ash. During this sampling period the Puertollano IGCC plant has been operated with close to 50:50 coal/pet-coke blends and 2.3–2.7% limestone addition (Table 1). In this power plant, the fuel, following pulverisation (down to <100 μm) and drying, is pressurised (to 25 bars) and carried to the gasifier in an inert environment of N_2. The pulverised fuel enters the gasifier through four burners set at 90 °C and is mixed with O_2 (85% purity). The gasification process is carried out at 1200–1600 °C and 25 bars. The slagging properties of the gasifier results in a high production (90%) of molten ash removed from the bottom of the gasifier in liquid form. The slag then enters a water bath, where is cooled and crushed. The remaining 10% of the ash is entrained by the gas. The fuel particles undergo the pyrolysis and gasification processes. The gases produced are first cooled down to 800 °C when leaving the gasifier with a recycled quenched gas flow (235 °C). When leaving the gasifier, the gas is successively cooled down to 400 and 265 °C in high and medium pressure boilers, respectively. In the pressure boilers high and intermediate pressure steam (127 and 35 bars, respectively) is produced, which is sent to the combined cycle heat steam regenerator boiler. After re-heating the steam is expanded into the steam turbine. The ashes are removed from the gas at 265 °C by means of ceramic candle filters. By this process the dust content of the gas is reduced to <3 mg/Nm^3. The gas, free of particles, is carried to the gas cleaning and desulphurisation unit. Halides and other impurities (HCl, HF, NH_3, HCN and H_2S) are removed from the gas using a Venturi scrubber with NaOH as a neutraliser agent. The sulphur is removed by conversion of H_2S to elemental sulphur. Then, the gas is expanded in a 200 MW gas turbine. A 135 MW steam turbine burns the steam generated in the heat recovery steam generator.

Table 1
Sampling date, limestone dose and coal/pet-coke ratio of the feed blends for the set of samples collected.

Sample set	Sampling date	Limestone (%)	Coal/pet-coke
#1	23/03/01	2.3	49.6/47.2
#2	25/05/05	2.7	44.2/52.9
#3	08/06/05	2.6	43.8/53.2
#4	20/10/05	2.5	46.0/51.5

The main chemical and mineralogical features of the feed fuel, slag and fly ash were investigated according to the following procedures:

- The moisture and ash content were determined at 105 and 750 °C following the ASTM recommendations.
- The content of major and trace elements were determined by means of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). A special two step sample digestion method for the analysis of potentially volatile elements in coals and fly ash devised by Querol et al. [15] was used to dissolve the samples prior to the analysis.
- Due the loss of silicon fluoride during the evaporation of HF from in the above sample digestion procedure, the HF acid digestion described by Thompson and Walsh [24] was used to determine the silica content in the bulk solid samples.
- The content of Hg was determined by Gold Amalgam Atomic Absorption Spectrometry (GA-AAS, AMMA-LECO) directly on solid samples.
- The Cl contents were determined by the Eschka method [25], followed by an ion chromatographic analysis of the water-leached residues.
- The determination of F was performed following the method described by Sager [26], and analysed by fluoride sensitive electrode.
- The contents of B were determined using the method described by Pougnet and Orren [27] and the resulting extracts analysed by ICP-AES.

- The amorphous and crystalline phases of the samples were determined by X-ray powder diffraction using a BRUCKER D5005 powder diffractometer with a graphite monochromator, NaI(Tl) detector, and Cu Kα radiation.

To quantify the partitioning among flue gas, fly ash and slag, Al-normalised EFs for major and trace elements in fly ash/feed fuel (EFfly ash) and slag/feed fuel (EF slag) as well as fly ash + slag/feed fuel or mass balance (MB) have been calculated considering Al as a non-volatile element during gasification using the following normalisation formulas proposed by Gordon and Zoller [28] and Querol et al. [15], (a) EFfly ash = [Ci – fly ash/CAl – fly ash]/[Ci – blend/CAl – blend], (b) EF slag = [Ci – slag/CAl – slag]/[Ci – blend/CAl – blend] and (c) MB = (EF fly ash * fly ash production) + (EF slag * slag production), were Ci is the concentration of a given trace element and CAl is the concentration of aluminium in the gasification by-product considered and in the fed fuel blend. The mass balance is obtained by normalising the EFs with the percentage produced of each by-product. The coal and coal-coke blend has been considered as the input stream and flue gas, fly ash and slag as the output streams. Using the above normalisation system, elements enriched in fly ash (by volatilisation followed by condensation from flue gas) will yield an enrichment factor (EFfly ash) > 1. Low volatile elements will not be enriched in fly ash, and will yield in an enrichment factor (EF slag) ⩾ 1. Low EFs for both fly ash and slag point to volatilisation processes with very minor condensation from flue gas. The MB, obtained from the adjusted EFs with the fly ash and slag production allows determining the volatile fraction of each element present in the raw gas. Mass balances <1 points to a partial gaseous phase in the raw gas for a given trace element. It is worth mentioning that an analytical error about 10–15% must be assumed in the determination derived from the method employed [29].

3. Results and discussion

3.1. Feed fuel characterisation and source of trace elements

The feed coal of Puertollano IGCC plant is characterised by low moisture (2.6–6.8%) and very high ash content (46–52%, Table 2). The ash content of the feed coal samples is higher than the range (11–36%) reported by Alastuey et al. [23] for coal bench characterisation, probably due to different coal seams being currently worked and because during mining some internal and external partings are also mixed with coal. The C contents range from 36% to 41% and H and N contents from 2.4% to 3% and from 0.5% to 0.9%, respectively (Table 2). The major mineral phases detected on the Puertollano feed coal samples are quartz, kaolinite, illite, siderite, ferric dolomite, dolomite and pyrite, in agreement with the mineralogy reported by Alastuey et al. [23]. The content of major and trace element determined in the feed coal samples from the sample sets (Tables 2 and 3) generally fall in the ranges obtained for the Puertollano coal by Alastuey et al. [23]. In specific samples, certain trace elements, such as As, Ba, Bi, Ni, U or V, slightly exceed the highest values reported by these authors. The contents of Cl (819–1424 mg/kg) and F (206–939 mg/kg) are reasonably high (six and three times higher than the coal worldwide values (180 and 88 mg/kg for Cl and F, respectively) reported by Yudovich and Ketris [30]. The high contents of Cl and probably also that of F of the Puertollano coal may be due to their accumulation in coals in a post-sedimentary digenetic process from leaching of the interlayered volcanic tuffs [31]. Among feed coal samples significant variations occur for S (0.4–1.0%), As (26–122 mg/kg), Ge (9–31 mg/kg), Ni (37–139 mg/kg), Pb (79–259 mg/kg), V (66–265 mg/kg), and Zn (260–515 mg/kg), such ranges probably being related to inter-seam or intra-seam geochemical variations reported by Alastuey et al. [23].

The pet-coke gasified at the Puertollano IGCC plant, is characterised by very low moisture (0.4–3.5%) and ash content (0.2–2.9%, Table 2) and by a very high C content (87.2–89.3%, Table 2). With the exception of the pet-coke sample from set #3, the S content is high (3.4–4.2% S, Table 3). Also pet-coke shows a high content of Cl (584–2013 mg/kg) and occasionally of F (up to 631 mg/kg in set #4, Table 3). With regard to metal content (Table 3), the pet-coke shows high contents of V (586–1236 mg/kg), Ni (199–301 mg/kg) and moderately high content of Mo (9.3–19.8 mg/kg) and Zn (<0.01–116 mg/kg). The results are in the range obtained for the pet-coke gasified at the Puertollano IGCC plant Puertollano [32].

The limestone used as fluxing aging has a C content close to 12% (Table 2). Since no organic C occurs (100% of C is extracted with HCl 5 N), the bulk C values are equivalent to a CO_3 content of 58.9%, 59.6%, and 55.1%. Besides calcite, traces of Fe-dolomite, quartz and clay minerals (such as montmorillonite) were also detected by XRD. The ratio calcite/dolomite is very high, ranging from 229 to 253 by weight. Taking into account this ratio, it can be assumed that >99% of Ca occurs as calcite, but when coupled with the geochemistry of the limestone samples (Tables 2 and 3) the calcite content ranges from 85% to >99%. The limestone samples are also

Table 2
Moisture, high temperature ashes (HTA), C, H, N and major oxide content (% db) in the feed coal, pet-coke, limestone and feed fuel blend for the sets of samples selected for this study (#1, #2, #3 and #4).

	Coal				Pet-coke				Limestone			Feed fuel blend			
Set	#1	#2	#3	#4	#1	#2	#3	#4	#2	#3	#4	#1	#2	#3	#4
Moisture	2.6	6.8	5.3	6.3	0.6	3.5	0.4	0.8	0.2	0.2	0.2	1.5	0.8	0.7	1.5
HTA	46	48	52	49	2.9	0.3	0.2	2.3	–	–	–	28	24	23	26
C	41	36	35	41	87	87	89	87	11.9	12.0	11.7	63	64	64	65
H	2.5	2.4	2.7	3.0	3.1	3.9	3.9	3.7	0.07	0.09	0.05	2.8	3.2	3.3	3.3
N	0.5	0.8	0.9	0.9	2.3	1.8	1.6	1.9	<0.01	<0.01	<0.01	1.4	1.4	1.2	1.4
Al_2O_3	11.4	11.4	12.4	11.1	0.1	0.1	0.1	0.05	0.8	1.0	0.6	5.7	5.6	5.7	4.8
CaO	0.4	0.5	1.0	0.3	0.03	0.07	0.03	0.03	48	52	55	1.3	0.9	1.0	1.4
Fe_2O_3	2.5	2.5	2.7	3.4	0.03	0.04	0.02	0.01	0.3	0.7	0.3	1.3	1.3	1.5	1.4
K_2O	1.2	1.1	1.1	1.1	0.01	<0.01	<0.01	<0.01	0.1	0.1	0.1	0.6	0.5	0.6	0.5
MgO	0.4	0.3	0.5	0.4	0.01	0.01	0.01	<0.01	0.6	0.6	0.5	0.2	0.2	0.2	0.2
MnO	0.03	0.02	0.02	0.03	<0.01	0.001	<0.01	<0.01	0.01	<0.01	0.01	0.01	0.01	0.01	0.01
Na_2O	0.02	0.1	0.3	0.8	<0.01	0.03	<0.01	0.04	0.01	0.03	0.01	0.01	<0.01	0.01	0.1
P_2O_5	0.03	0.04	0.5	0.1	<0.01	0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.02	<0.01	0.01	0.03
SiO_2	24	24	27	25	0.2	0.3	<0.01	0.7	1.5	1.4	2.3	12.1	10.3	9.6	11.1
S	0.9	0.4	0.5	1.0	3.4	4.2	0.1	3.9	0.04	0.2	0.04	2.6	1.0	1.1	2.4
TiO_2	0.3	0.3	0.4	0.3	<0.01	<0.01	<0.01	<0.01	0.03	0.1	0.02	0.2	0.1	0.2	0.1

Table 3
Trace element contents (in mg/kg, d.b., except for Hg, μg/kg, d.b.) in the feed coal, pet-coke, limestone and feed fuel blend for the sets of samples selected for this study (#1, #2, #3 and #4).

	Coal				Pet-coke				Limestone			Feed fuel blend			
Set	#1	#2	#3	#4	#1	#2	#3	#4	#2	#3	#4	#1	#2	#3	#4
Cl	819	1424	894	1024	2013	1447	584	865	2017	2017	<500	1714	1363	1237	300
B	45	31	52	47	14	11	22	20	21	24	33	29	26	29	33
F	232	206	269	934	23	36	27	631	89	111	625	125	122	124	717
Br	–	10.5	10.8	9.5	–	3.5	2.2	1.8	0.1	–	–	–	7	6.5	5.7
I	–	1.4	7.2	6.1	–	1.5	2.7	2.3	3.3	–	–	–	1.5	5	4.2
As	61	66	26	122	1.5	1.4	0.7	2.8	3.3	14.4	2.1	31	33	22	22
Ba	209	293	238	309	2.0	5.7	3.2	4.1	18	26	21	135	144	140	125
Be	3.0	5.4	4.2	3.8	0.4	<0.01	0.1	<0.01	0.4	0.4	0.1	2.7	2.1	1.9	1.7
Bi	2.4	<0.01	1.6	1.2	2.1	<0.01	<0.01	0.1	<0.01	0.1	0.1	0.4	0.1	1.1	0.8
Cd	2.8	1.0	1.6	0.8	1.9	<0.01	0.03	0.1	<0.01	0.1	0.1	0.6	0.6	0.8	0.7
Co	16	18	15	14	0.7	2.4	0.8	0.8	5.0	1.9	1.3	6.1	9.4	8.2	6.4
Cr	61	50	48	43	10.9	7.2	3.2	5.0	10.3	7.8	5.7	26	28	28	24
Cs	45	29	21	31	<0.01	<0.01	0.2	0.05	<0.01	0.8	0.4	20	14	15	13
Cu	44	48	44	56	1.8	4.6	1.7	1.9	0.8	4.4	2.9	16	21	20	17
Ga	9	16	18	16	0.3	0.9	1.0	0.7	1.3	1.5	0.9	4.9	9.1	10.5	8.1
Ge	16	9	12	31	<0.01	<0.01	0.4	1.1	<0.01	0.4	0.2	6.6	8.1	8.3	11.3
Hf	3.8	4.0	8.7	11.3	1.4	2.5	0.02	0.1	2.3	1.0	0.4	1.7	1.6	5.1	3.8
Hg	523	571	404	400	9	42	15	6.9	3.8	7.9	2.2	0.2	0.3	0.2	0.2
La	30	24	23	24	0.2	0.6	0.3	0.1	1.8	2.4	1.6	18	12	14	11
Li	60	89	70	88	0.6	<0.01	0.4	3.0	3.9	4.5	3.0	38	44	35	40
Mo	7.5	7.9	1.8	5.1	11.8	19.8	8.8	9.3	0.9	<0.01	<0.01	7.6	11.9	7.5	5.8
Nb	9.3	17.1	7.8	7.5	<0.01	<0.01	<0.01	0.02	<0.01	0.8	0.7	5.0	5.1	4.5	3.7
Ni	37	139	38	41	219	301	199	285	34	9.5	6.2	123	216	128	135
Pb	250	160	188	79	2.2	3.3	1.4	1.4	3.3	3.6	1.9	140	95	117	120
Rb	61	51	61	53	0.2	<0.01	0.2	0.2	4.0	6.5	3.9	29	27	35	25
Sb	40	42	21	48	5.6	<0.01	0.1	1.6	<0.01	0.3	0.4	20	20	15	24
Sc	7.7	8.0	44	80	0.4	1.0	0.7	<0.01	1.4	5.6	1.8	4.5	3.9	22.5	15.8
Se	<0.01	<0.01	1.4	<0.01	<0.01	1.3	<0.01	<0.01	0.4	1.1	<0.01	3.0	0.7	2.9	2.4
Sn	2.9	4.6	3.8	3.4	0.3	1.1	<0.01	0.2	1.1	0.3	0.4	1.9	2.8	2.2	1.8
Sr	44	51	65	50	0.6	1.8	1.4	1.5	126	113	142	28	29	35	30
Ta	4.6	17.2	1.0	2.1	1.7	2.7	0.02	0.04	5.9	0.1	0.05	1.5	2.5	0.4	0.6
Th	4.2	9.1	11.2	11.7	1.1	6.3	0.03	0.03	7.6	0.8	0.5	7.2	5.5	5.6	4.3
Tl	1.2	4.1	0.8	1.0	1.0	3.9	<0.01	0.01	4.6	0.1	0.03	0.5	2.5	0.6	0.4
Tm	0.5	1.1	0.4	0.3	0.2	0.7	<0.01	0.01	0.8	0.03	0.02	3.6	5.4	2.0	1.7
U	2.6	13.6	4.0	3.6	1.9	6.8	0.02	0.04	8.3	0.4	0.4	855	734	415	558
V	72	265	66	72	849	1237	586	1235	1.3	15.1	5.8	3.5	7.1	1.9	2.2
W	12.3	21.7	2.6	10.0	2.3	10.8	0.04	1.8	9.2	0.1	0.8	11.5	8.7	12.7	10.3
Y	21	19	25	23	<0.01	0.9	0.1	0.1	2.1	2.7	1.6	130	281	246	240
Zn	271	458	515	260	<0.01	116	27	29	12	18	11.4	48	30	39	29
Zr	52	50	59	93	<0.01	3.2	0.02	1.1	4.1	8.1	3.4	27	12	8	21

characterised by relatively high contents of Cl (up to 2017 mg/kg) and F (89–625 mg/kg). These elements may occur in the apatite framework, a mineral commonly found in limestone, but other Cl and F species should occur in limestone taking into account that apatite is not present in XRD detectable levels (<1% wt of apatite, if any).

In accordance with the contents determined for coal, pet-coke and limestone, the feed fuel blend is characterised by a low moisture (0.7–1.5%), high ash (23–28%) and high C contents (63–35%, Table 2). Despite the dilution effect of the addition of pet-coke, the feed fuel still contains relatively high contents of S (1.0–2.6%) and the trace elements enriched in coal and pet-coke. The content of Cl, F, I, Bi, Ga, Hf, Mo, Ni, Sc, Se, Tl, U, V, W, Zn and Zr show significant variations among set of samples (by a factor of 2–5), whereas the variations found for other trace elements in coal and pet-coke are masked by the dilution effect (Tables 2 and 3).

As regards the relative contributions of coal, pet-coke and limestone to the major and trace elements in the feed fuel blend (Fig. 1), coal is the main source (>80%) for most elements (Al, Fe, K, Mg, Na, Si, Ti, As, Ba, Be, Co, Cs, Cu, Cr, Ga, Ge, Hg, Li, Nb, Pb, Rb, Sb, Sc, Sn, Sr, Y, Zn and Zr). With the exception of Mg and Sr, the remaining proportion of these elements is provided by pet-coke. Due to the high V and Ni contents and the high proportion of pet-coke in the feed fuel blends, this secondary fuel is the main source of Ni (68–87%), V (82–94%) and Mo (65–83%). Commonly, a high proportion of S is sourced from pet-coke (79–91%), although in some cases it can derive mainly from coal (84% set #3). As expected, Ca is supplied mainly from the limestone (72–91%). Even with low amounts of limestone with respect coal and pet-coke, this material provides significant proportions of Mg (6–8%) and Sr (8–12%) to the feed fuel blend. Coal is usually the main source of B and F (around 70 and 59–89%, respectively), but a significant fraction, around 30% of B and 9–39% of F is supplied by pet-coke. Chlorine is supplied in similar proportions by coal (48–56%) and pet-coke (37–49%), respectively. A number of elements show a relatively high variability in the proportions supplied by coal and pet-coke. In this regard, although coal supply up to >95% of P, Mn, Bi, Hf, Ta, Th, Tl, U and W, pet-coke can also supply significant amounts of these elements (21–49%). The highest proportions supplied by pet-coke of P, Bi, Hf, Ta, Th, Tl, U and W occurs for set #2 while that of Mn for set #3. The source of Se also shows a high variability, being supplied in high proportions (75%) by coal in sets #3 and #4 and by pet-coke in set #2 (68%).

3.2. Slag and fly ash characterisation

The slag is mainly made up of an amorphous Al–Si glass (>99%). Anorthite ($CaAl_2Si2O_8$), clinoferrosilite ($FeSiO_3$), orthoferrosilite ($(Fe, Mg)SiO_3$) and Al–chromite Fe $(Al,Cr)_2O_4$) may crystallize from the melt if cooling is slow enough [22] The SiO_2 and Al_2O_3 contents

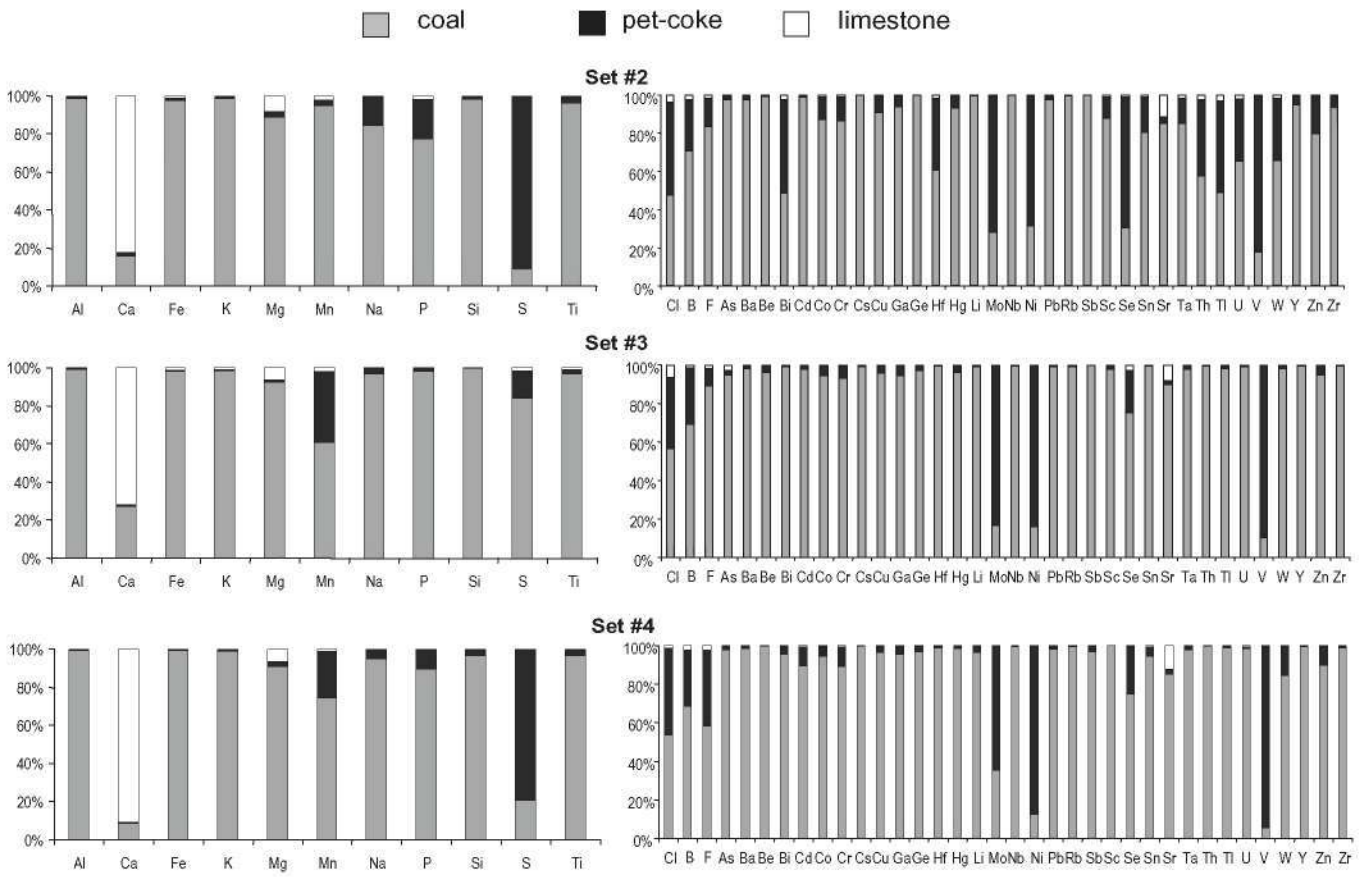

Fig. 1. Relative contribution of coal, pet-coke and limestone to the bulk content of major (right) and trace elements (left) of the feed fuel blend of the Puertollano IGCC plant in three feed sample sets.

in the slag range from 50.2% to 59.2% and from 23.0% to 24.5%, respectively (Table 4). The slag samples also contains minor amounts of Fe_2O_3 (4.5–7.4%), CaO (4.9–7.5%) and SO_3 (1.0–2.4%) contents. Furthermore, high contents of a number of minor and trace elements, such as V (1681–3527 mg/kg), Ni (192–828 mg/kg), Cl (200–1392 mg/kg) and occasionally in F (548 mg/kg in sample S-#13) were also determined (Table 4).

As regards Puertollano IGCC fly ash samples, the speciation of a number of trace elements are similar than reported in previous studies [21,22,32–34]. These studies revealed that IGCC fly ash samples are mainly made up of an amorphous Al–Si glass The crystalline phases galena (PbS), sphalerite and wurtzite (ZnS) and phyrrhotite ($Fe_{1-x}S$), as well as nickeline (NiAs), condensed from reducing vapour species in cooling flue gas, are present in XRD detectable levels (>1% wt). Table 4 shows the concentrations of major and trace elements in the IGCC fly ash samples. The concentration of Zn, Pb, Ge, As, Sb, Cd, Cu, Sn, V, Ni, and Mo, in fly ash are around one order of magnitude higher than the highest concentrations of fly ash from PCC European plants while SiO_2 concentrations are close to maximum concentrations observed in 23 European combustion fly ash [35]. As shown in Table 5, a large number of elements (Pb, Ge, Ga and Bi As, Br, Sb, B, F, Cd, Tl, Se, Zn, Sn) display extremely high fly ash/slag ratios when compared with usually obtained in coal combustion [14,15]. The mean values for the four set of samples are in the range of 9–568. This is due to the high slag production with respect fly ash (90:10) and the high occurrence of condensation processes during gas cooling [21]. Other elements typically highly volatile (S, Hg, I, and Cl) show mean fly ash/slag ratios in the 0.7–2.1 range. Copper, W, Mo, Ni and Na show fly ash/slag ratios ranging from 1.5 to 6.3 while the usually low volatile elements display fly ash/slag ratios ranging from 0.4 to 2, respectively.

The high enrichment of IGCC fly ash in the above elements may be attributed to the following major causes: (a) the high slag/fly ash ratio of the entrained flow gasifiers compared with pulverised coal combustion (90:10) accounts for the high content of condensing material (with a high proportion of partially volatilised elements) with respect to the non-volatile Al–Si glass. In absolute values the total amount of metals and semi-metals present in gasification and combustion by-products (slag and fly ash) is similar, or even lower in IGCC (vs. PCC) since a lower proportion of coal is used in the feed fuel; (b) the use of petroleum coke with high V and Ni contents in the IGCC and; (c) the relatively high contents of Pb, Sb, Zn and other trace elements in the Puertollano coal when compared with other world wide coals.

3.3. Partitioning of major and trace elements

The partitioning of trace elements allowed to the following classification for major and trace elements according to their volatile behaviour during co-gasification of coal and pet-coke in a entrained flow gasifier:

- High volatile elements (70–99% in gas phase): Hg, Cl and S.
- Moderately volatile elements (up to 40% in gas phase and $\geqslant$60% in fly ash): As, Sb, B, F, Cd, Tl, Se, Zn and Sn.
- Elements with high condensation potential: (>90% in fly ash): Pb, Ge, Ga and Bi.
- Elements enriched similarly in fly ash and slag (30–60% in fly ash): Cu, W, (P), Mo, Ni and Na.

Table 4
Content of C, major oxides (%) and trace elements (mg/kg, db) of the slag (S) and fly ash (FA) samples of the sample sets selected for this study.

	S#1	S#2	S#3	S#4	FA#1	FA#2	FA#3	FA#4
C	0.4	0.2	2.4	4.0	3.8	5.5	2.3	2.8
Al_2O_3	24.5	26.0	24.9	23.0	22	19	20	19
CaO	7.5	5.4	4.9	7.0	3.1	3.5	3.5	3.2
Fe_2O_3	4.5	7.4	7.0	6.2	4.6	4.8	4.8	5.0
K_2O	1.9	2.2	2.2	2.1	3.7	3.8	4.0	4.1
MgO	1.0	0.6	0.9	1.0	0.6	0.7	0.8	0.7
MnO	0.1	0.1	0.1	0.1	–	0.03	0.01	0.04
Na_2O	<0.01	0.3	0.3	0.3	0.5	0.5	0.2	0.6
P_2O_5	0.0	<0.01	0.1	0.1	0.5	0.7	–	0.7
SiO_2	59.2	51.8	50.5	50.2	57	52	54	56
SO_3	1.0	2.4	2.1	1.7	2.8	3.5	3.0	3.3
TiO_2	0.6	0.7	0.8	0.7	0.6	0.6	0.7	0.6
mg/kg								
Cl	858	1372	653	500	<500	823	353	500
B	44	42	51	66	<500	453	471	519
F	43	54	62	548	2811	2845	3298	3816
Br	–	<0.1	<0.1	<0.1	–	40.8	24.5	28.5
I	–	<0.1	<0.2	1.7		70.6	47.2	53.0
As	7.3	9.4	9.3	7.0	677	621	613	707
Ba	607	647	645	574	386	424	440	421
Be	10.9	9.2	8.1	7.3	14	10	10	9
Bi	0.7	<0.01	0.03	0.03	8	1	8.0	6.8
Cd	0.4	<0.01	0.3	0.2	17	17	22	20
Co	23	40	34	27	56	43	39	40
Cr	99	121	123	100	163	124	123	195
Cs	61	51	52	47	185	127	149	133
Cu	28	56	56	40	353	326	269	334
Ga	0.9	3.0	3.0	2.4	247	262	306	264
Ge	0.2	0.0	1.1	0.5	232	238	255	377
Hf	7.3	7.4	21.6	18.2	8	6	5.6	4.3
Hg (μg/kg)	2.2	2.3	1.3	1.2	0.3	1.2	2.4	4.8
Li	156	196	143	171	156	186	171	233
Mo	17	41	25	16	137	113	82	94
Nb	20	21	20	18	28	25	19	15
Ni	342	828	450	460	2153	1809	1031	1621
Pb	6	6	5	8	3405	2855	3595	4063
Rb	103	108	132	102	282	209	264	208
Sb	4.5	<0.01	1.9	2.0	412	415	461	544
Sc	21	18	95	77	114	13	85	67
Se	8.0	0.3	0.4	0.3	4	6	11	7
Sn	1.2	1.3	0.4	0.5	64	59	64	54
Sr	124	133	154	135	99	114	120	118
Ta	7.0	11	1.7	2.9	8	10	2	2
Th	30	25	25	21	22	18	21	17
Tl	<0.01	7.4	0.1	0.1	15	19	16	13
U	15	25	8	8	15	20	11	9
V	3444	2852	1681	2267	5591	5245	2813	4916
W	8	22	5	6	59	81	29	35
Y	51	43	54	47	43	27	42	35
Zn	13	13	25	22	5785	6242	6540	7788
Zr	211	141	175	147	147	106	126	101

- Low volatile elements (>70% in the slag): Cs, Rb, Co, K, Cr, V, Nb, Be, Hf, Ta, Fe, U, Ti, Al, Si, Y, Sr, Th, Zr, Mg, Ba. Mn, REEs, Ca and Li.

The calculated EFs (Table 5) revealed that highly volatile elements are generally depleted in fly ash and slag with EF fly ash ranging from <0.01 to 1.5 and EF slag from <0.01 to 0.4. The moderately volatile elements and the elements with high condensation potential show high EF fly ash (2.2–10.2 and 6.2–10.4, respectively) and are depleted in slag, with low EF slag (0.03–0.6 and 0.01–0.4, respectively). The elements enriched similarly in fly ash and slag show similar EFs in fly ash and slag but P and Na may show enrichment in fly ash at low limestone dosages. The low volatile elements show EF_{FA} close to 1, but specific elements (such as K, V, U, Co, Cr, Fe, Si, Ti, Rb) may be slightly enriched in fly ash (EF_{FA} = 1.3–2.3) at low limestone dosages (K, Co, Fe, Si, Cr, Ti, Mo and Rb) and high pet-coke addition (V and U).

3.3.1. High volatile elements

This group includes the high volatile Hg, Br, I, Cl and S. These elements partially volatilise during gasification and remain in high proportions in the gas phase at fly ash removal temperatures (265 °C), pointing out the occurrence of species with low boiling points. Thus, Hg most probably occurs as high volatile [11] Hg^0, which accounts for the high proportions (>99%) of this metal in gas phase at fly ash removal temperatures (Fig. 2). The low proportions of Hg retained in fly ahs may be related to the occurrence of Hg_2Cl_2. The high positive correlation among Ca and Hg (R^2 = 0.96, with the exception of set #4) and low negative correlation between C and Hg (R^2 = 0.33) contents in fly ash suggest that Hg_2Cl_2 is adsorbed by CaO rather than for char particles as reported by other authors [36]. The high volatile character of Br and I bearing species [37], most of them having boiling points <184 °C, account for their high proportions in gas phase (>98% and 85–89%, respectively, Fig. 2) at fly ash removal temperatures, despite the major associa-

Table 5
Enrichment factors for slag (EF slag) and fly ash (EFfly ash) and mass balances (MB) for the sample sets investigated.

	Fly ash/slag ratio				EF slag				EF fly ash			
	#1	#2	#3	#4	#1	#2	#3	#4	#1	#2	#3	#4
Al	0.9	0.7	0.8	0.8	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ca	0.4	0.6	0.7	0.5	1.0	1.0	1.1	1.0	0.6	0.6	0.6	0.6
Fe	1.0	0.6	0.7	0.8	0.9	1.0	1.0	1.0	1.4	0.9	0.9	1.0
K	1.9	1.7	1.8	2.0	0.9	0.9	0.8	0.9	2.3	2.3	2.0	2.0
Mg	0.6	1.2	0.9	0.7	0.9	1.0	1.0	1.0	1.2	0.8	0.8	0.9
Mn	–	0.3	0.1	0.4	0.9	1.0	1.0	1.0	1.4	0.8	0.7	0.9
Na	>50	1.7	0.7	2.0	0.8	0.2	0.9	0.9	2.6	1.1	1.8	1.8
P	–	–	–	7.0	0.2	0.9	0	0.4	8.1	2.1	10.1	6.1
Si	1.0	1.0	1.1	1.1	1.1	0.9	1.0	1.0	1.0	1.0	1.3	1.3
S	2.8	1.5	1.4	1.9	0.03	0.1	0.3	0.1	0.1	0.3	0.4	0.1
Ti	1.0	0.9	0.9	0.9	1.0	1.0	1.0	1.0	1.3	1.2	1.0	1.0
Cl	0.6	0.6	0.5	1.0	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1
B	>11	11	9.2	7.9	0.4	0.3	0.4	0.4	4.9	4.9	4.5	4.0
F	65	53	53	7	0.1	0.1	0.1		6.7	6.5	7.3	–
Br	–	408	245	285	–	<0.01	<0.01	<0.01	–	1.4	1.5	1.5
I	–	706	236	31	–	<0.01	<0.01	<0.01	–	0.2	0.2	0.2
As	93	66	66	101	0.1	0.1	0.1	0.1	5.9	5.3	7.6	9.4
Ba	0.6	0.7	0.7	0.7	1.1	1.0	1.1	1.0	1.0	0.8	0.9	0.9
Be	1.3	1.1	1.2	1.2	0.9	0.9	1.0	1.0	1.0	1.0	1.4	1.4
Bi	11	100	267	227	0.4	0.01	0.01	0.01	6.2	10.4	9.7	9.6
Cd	43	1700	73	100	0.2	<0.01	0.1	0.1	7.1	9.4	8.4	7.4
Co	2.4	1.1	1.1	1.5	0.9	0.9	1.0	0.9	1.7	1.3	1.3	1.6
Cr	1.6	1.0	1.0	2.0	0.9	0.9	1.0	0.9	1.6	1.2	1.2	2.1
Cs	3.0	2.5	2.9	2.8	0.7	0.8	0.8	0.8	2.9	2.5	2.7	2.7
Cu	13	5.8	4.8	8.4	0.4	0.6	0.7	0.5	5.8	4.3	3.9	5.0
Ga	274	87	102	110	0.04	0.1	0.1	0.1	9.8	8.9	9.3	8.9
Ge	1160	–	232	754	0.01	<0.01	0.04	0.01	9.6	9.9	9.7	9.9
Hf	1.1	0.8	0.3	0.2	1.0	1.0	1.0	1.0	1.1	1.1	0.9	0.9
Hg	0.1	0.5	1.8	4.0	0.003	0.001	0.002	0.001	0.001	0.002	0.003	0.006
Li	1.0	0.9	1.2	1.4	1.0	1.0	0.9	0.9	1.6	1.2	1.3	1.5
Mo	8.1	2.8	3.3	5.9	0.5	0.7	0.8	0.7	5.2	2.7	3.2	4.5
Nd	1.4	1.2	1.0	0.8	1.0	1.0	1.0	1.0	0.8	0.8	0.9	0.8
Ni	6.3	2.2	2.3	3.5	0.7	0.8	0.8	0.7	4.6	2.4	2.2	3.1
Pb	568	476	719	508	0.01	0.02	0.01	0.02	9.1	9.9	9.9	9.4
Rb	2.7	1.9	2.0	2.0	0.8	0.9	0.9	0.9	2.4	2.3	2.1	2.1
Sb	92	–	243	272	0.1	<0.01	0.03	0.03	5.4	5.7	9.0	10.2
Sc	5.4	0.7	0.9	0.9	1.1	1.0	1.0	1.0	0.8	1.0	1.0	1.1
Se	0.5	20	28	23	–	0.1	0.2	0.1	–	6.9	8.9	8.6
Sn	53	45	160	108	0.2	0.1	0	0.1	8.6	5.9	9.2	8.5
Sr	0.8	0.9	0.8	0.9	1.0	1.0	1.0	1.0	1.1	1.1	0.9	1.0
Ta	1.1	0.9	1.2	0.7	1.1	0.9	1.0	1.0	0.5	1.1	1.1	1.0
Th	0.7	0.7	0.8	0.8	1.0	1.0	1.0	1.0	0.9	0.9	1.0	1.0
Tl	1500	2.6	160	130	<0.01	0.6	0.05	0.04	7.5	2.2	9.1	7.8
U	1.0	0.8	1.4	1.1	1.0	1.1	1.0	1.0	1.2	1.1	1.5	1.4
V	1.6	1.8	1.7	2.2	0.9	0.8	0.9	0.9	1.7	2.0	1.9	2.2
W	7.4	3.7	5.8	5.8	0.5	0.7	0.6	0.6	5.7	3.5	4.4	4.2
Y	0.8	0.6	0.8	0.7	1.0	1.1	1.0	1.0	1.0	0.9	0.9	0.9
Zn	445	480	262	354	0.02	0.01	0.02	0.02	9.9	6.2	7.3	9.9
Zr	0.7	0.8	0.7	0.7	1.0	1.0	1.0	1.1	1.0	1.0	0.9	0.9

tion with the coal ash components than with the organic matter of coal (Tables 2 and 3).The proportion of Br and I retained in fly ash may be related to unburned pet-coke particles containing Br and I as suggested by the simultaneous increase of these elements and unburned C in fly ash (Table 4). The association of Br organically-bound in coal, with char particles in fly ash was also suggested in studies on the behaviour of this element during coal combustion [38]. Nevertheless, the occurrence of less volatile Br bearing species, such as NaBr, cannot be rule out.

The proportion of Cl and S in gas phase ranges from 88 to >99% and 68 to 96%, respectively (Fig. 2). The remaining Cl and S are distributed in slag rather than in fly ash (Fig. 2). Since the volatile fraction of Cl correlates negatively with the Cl content in the feed coal (R^2 = 0.79), the high volatility of Cl is probably due to the high content of organic Cl arising from pet-coke. In the feed coal, Cl most probably occurs in refractory phosphate minerals, such as apatite, rather than to organic matter, as suggested by the high correlation of Cl with U (R^2 = 0.93), Be (0.82) and Li (0.64), elements with phosphate and Al–Si affinity in the Puertollano coal [23]. The occurrence of these low volatile Cl species may partially account for the considerable proportions of Cl retained in the slag. The positive trend between Cl and Al (R^2 = 0.76), U (0.98) and REE's (0.80) in the slag samples suggest that most of the Cl bound to refractory minerals of coal, may be dissolved and retained in the Al–Si melt (process controlled by diffusion in the melt) or retained as fluid inclusions, as reported for coal combustion [38]. In this regard, the level of limestone dosage seems to be the most important feed parameter affecting Cl and S volatility, as suggested by the negative correlation between the limestone content in the feed fuel blend and the Cl and S volatile fractions (R^2 = 0.91 and 0.38, respectively). High limestone content reduces the volatile fraction of Cl and S while increases their enrichment in slag. For Cl, high Ca contents may favour the above mentioned dissolution in the A–Si melt. In summary, both, the high R^2 correlation factors of Cl content with Al, U and REEs in the slag, which in turn are associated with Zr, supports that the partial occurrence of Cl in refractory minerals

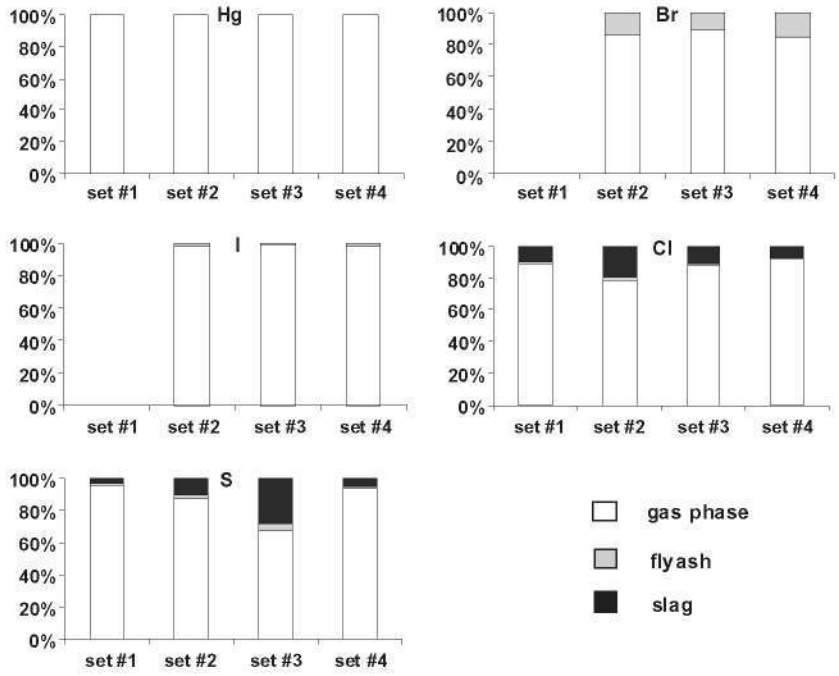

Fig. 2. Normalised mass balance for high volatile elements (>70% in gas phase).

in the Puertollano coal and the trapping of Cl in melt, especially at high Ca dosages are the most important causes for retaining Cl in the slag reducing its volatile fraction. For S, the enrichment in slag rather than in fly ash is attributed to the formation of pyrrhotite–millerite ($Fe_{1-x}S$–NiS) when increasing limestone content. The occurrence of these sulphide species in the slag is deduced from the high correlation (R^2 = 0.6–0.8) between limestone content and those of sulphide bearing elements (S, Fe, Ni, Mo, Cu and Co).

3.3.2. Moderately volatile elements (up to 40% in gas phase and ⩾60% in fly ash)

This group of elements includes As, Sb, Se, B, F, Cd, Tl, Se, Zn and Sn. High proportions of these elements volatilise during gasification [11], and partially condense during the flue gas cooling. However, a significant proportion of those may remain in gas phase at fly ash removal temperatures. Within this group the following subgroups can be differentiate as a function of the proportion in gas phase (Fig. 3):

- 50–90% in fly ash and up to 43% in gas phase: includes As (<0.01–42% in gas phase), Sb (<0.01–43%), Zn (0–37%) and Sn (<0.01–32%).
- >65% in fly ash up to 25% in gas phase: Cd (6–20%), Tl (5–32%) and Se (0–23%).
- Up to 21% in gas phase: B (17–20%) and F (18–21%).

The levels of volatile Cl and the limestone content of the feed fuel blend account for the variability of the proportions of As, Sb, Zn, Sn, Cd, Tl and Se as gaseous species. Thus, the proportions of As, Sb, Tl and Se in gas phase at fly ash removal temperatures increased as Cl content in pet-coke increases An increased content of gaseous Cl may favours a high occurrence of high volatile As, Tl, Sb and Se chloride species, such as $AsCl_3$ (boiling point 130 °C), $SbCl_3$ (220 °C), $SnCl_5$ (140 °C), $TlCl_3$ (155 °C) and Se_2Cl_2 (127 °C) [37]. Conversely, the volatile proportions of Zn, Sn and Cd are reduced when the limestone content in the feed fuel blend increases. As previously stated, low proportions of Cl levels in the gas phase are caused by high limestone dosages. Under these conditions the condensation of Zn, Sn and Cd sulphides is favoured rather than the formation of gaseous chloride species [11], such as $ZnCl_2$. Furthermore, the proportion of As and Sb in gas phase could be also controlled by the levels of Ni in the feed fuel [39], available to form nickeline–brethautite in this gasification fly ash. The high organic affinity of B (60% of the bulk B) in the feed coal [14,15] and, in pet-coke (close to 100%) accounts for the high volatility of this element in IGCC. As reported by several authors [14,15,40] the mode of occurrence of B in coal is controlling its volatile behaviour during combustion. The occurrence of B in tourmalines or other silicate minerals reduce the volatility, whereas a mainly organic affinity favours the occurrence of B in the gas phase. In a similar way the mode of occurrence of F in the feed fuel controls the release of this element to the gas phase. In the feed coal of Puertollano IGCC plant, P (R^2 = 0.81) and Al–Si affinity is deduced for F, suggesting a major occurrence in apatite or in silicates. Therefore, the F organically-bound in pet-coke should be the major source for volatile F.

Although a highly volatile proportion of B and F is available, only small proportions of these elements (up to 21% and 25%, respectively) remain in the gas phase at fly ash removal temperatures (Fig. 3). B is retained in fly ash (40–49%) rather than in slag (31–38%, Fig. 3). Probably volatile B occurs as oxide species (B_2O_3),[11] which is retained in fly ash by the condensation and/or adsorption on the Al-rich fly ash particles as suggested by other authors [33,40] and supported by the correlation between B and Al contents (R^2 = 0.60) in Puertollano IGCC fly ash. The main causes for retaining B in the slag are probably the low volatility of B bearing silicates in coal, which may give rise to retain B in the Al–Si glass matrix of the slag, and the high affinity of B to Ca to form Ca borates, such as takaidite ($Ca_3B_2O_6$), especially in reducing environments [39].

F is mainly occurring in fly ash (65–73%) and only a small proportion (7–10%) is retained in the slag. This partitioning may be the result of partial condensation of volatilised F during gas cooling. The relatively high correlations factors among contents of F and

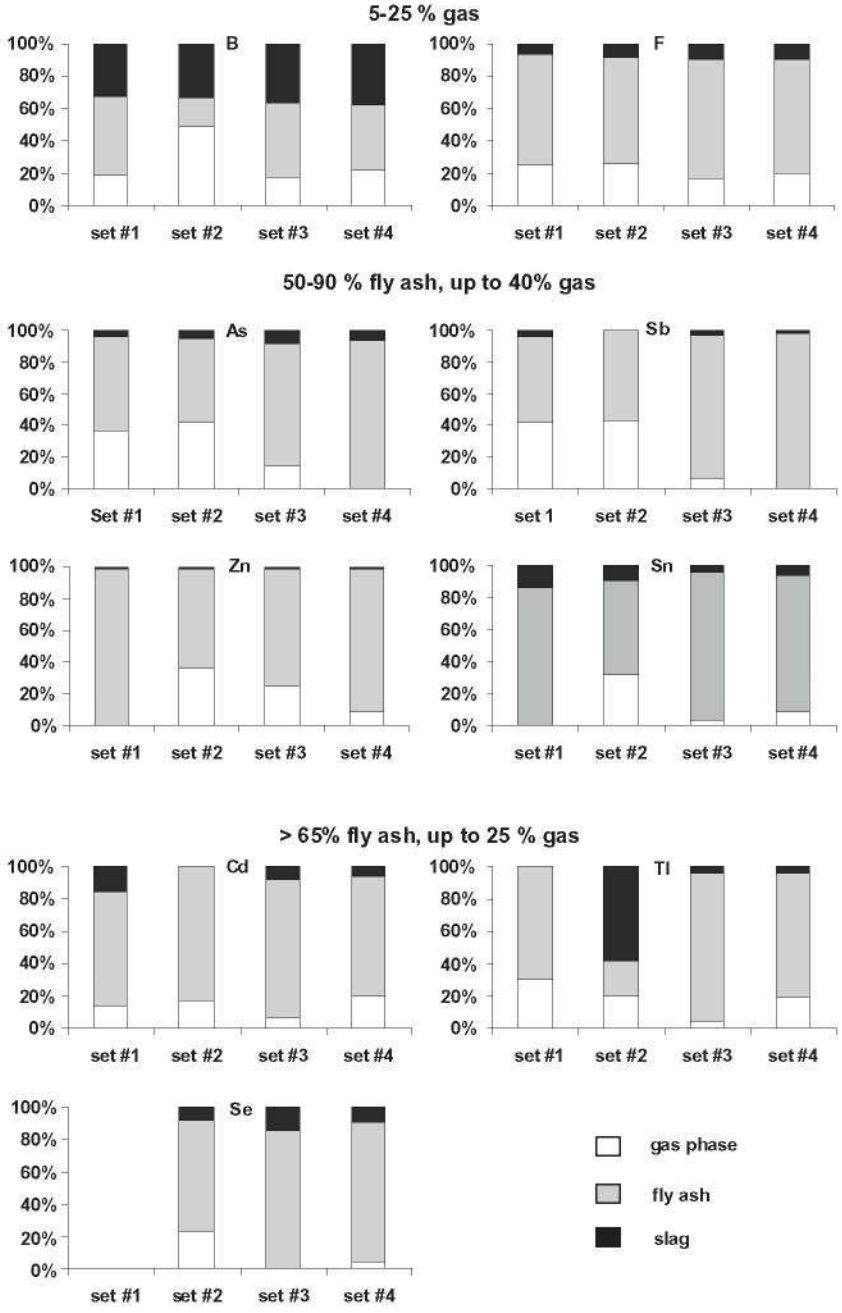

Fig. 3. Normalised mass balance for relatively high volatile (up to 40% in gas phase).

K, Sr and Na in fly ash suggest the formation of K–Na–Sr fluoride species during gasification as the main cause for the high retention of this element in fly ash.

3.3.3. Elements with high condensation potential: (⩾90% in fly ash): Pb, Ge, Ga and Bi

This group includes elements that are partially volatilised during gasification and subsequently condense during gas cooling to form sulphide and oxide species. The complete volatilisation of these elements is caused by the high organic occurrence of Ge and the major sulphide affinity of Pb, Ga and Bi in the Puertollano coal [23]. The high chalcophile affinity of these elements in reducing conditions account for the formation of sulphide species, such as galena for PbS, GeS and GeS_2 for Ge or substituting for Zn in sphalerite/wurtzite lattices for Ga, and the consequent high retention of these elements in fly ash (Fig. 4).

Elements enriched similarly in fly ash and slag (30–60% in fly ash): Cu, W, (P), Mo, Ni and Na. This group of elements includes Cu, W, Mo, Ni and Na, with proportions retained in fly ash ranging from 40–60%, 40–60%, 30–50%, 20–50% and 20–40%, respectively (Fig. 5). Phosphorus is included in this group although the partitioning between slag and fly ash vary from 20% to 100% (Fig. 5). The limestone addition controls the enrichment of these metals and semi-metals in slag and fly ash, being enriched in slag rather than in fly ash for the highest limestone dosages, with correlation factors between limestone and the EF fly ash ranging from 0.70 to 0.99.

3.3.4. Low volatile elements (⩾70% in the slag)

This group of elements includes Cs, Rb, Co, K, Cr, V, Nb, Be, Hf, Ta, Fe, U, Ti, Al, Si, Y, Sr, Th, Zr, Mg, Ba. Mn, REEs, Ca and Li, being highly (>70%) concentrated in the slag. The high retention of these

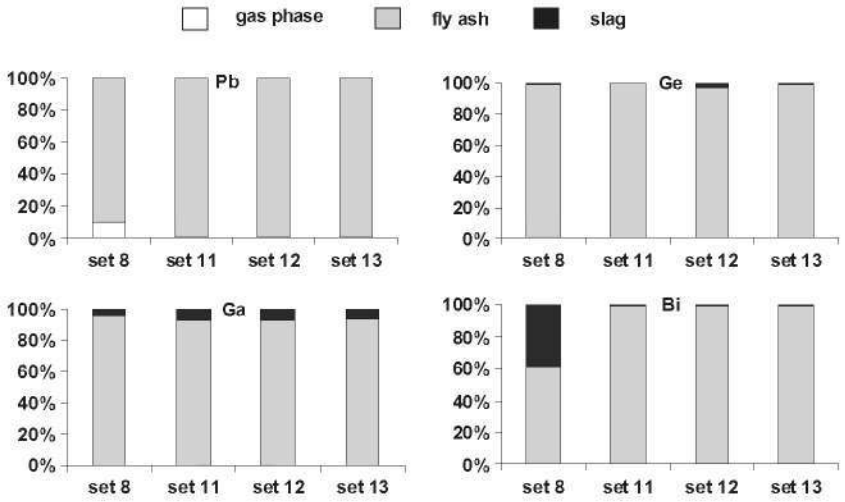

Fig. 4. Normalised mass balance for elements with high condensation potential.

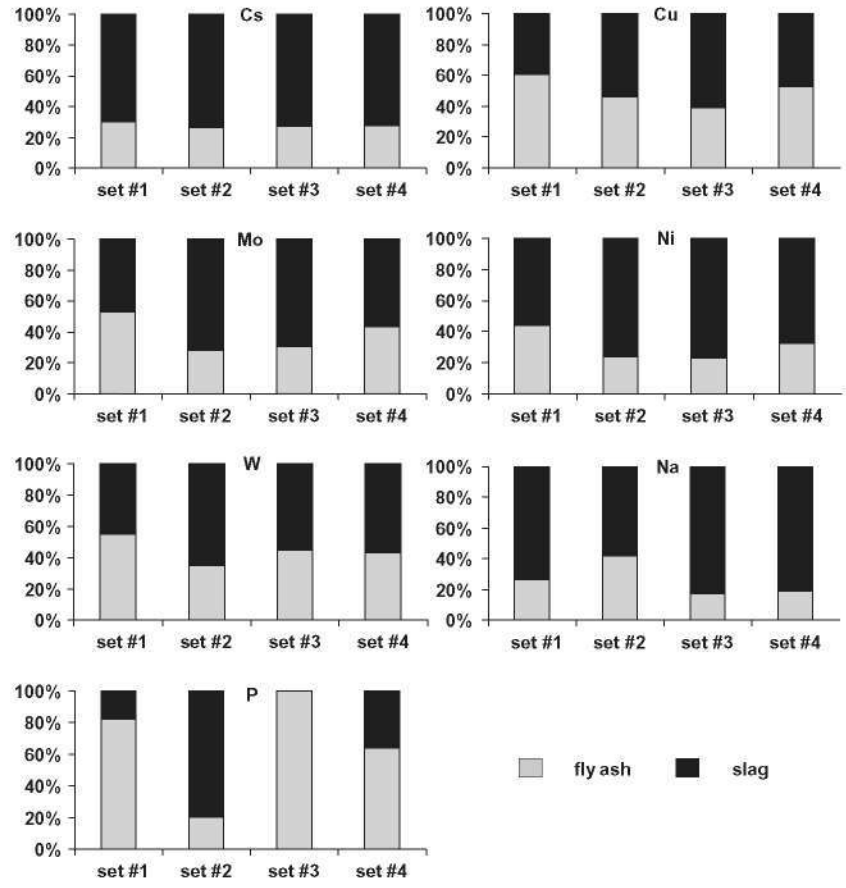

Fig. 5. Normalised mass balance for elements enriched similarly in fly ash and slag (30–60% in fly ash).

elements in the slag is due to the high slagging conditions of the Puertollano plant favoured by the addition of limestone as a fluxing agent in the feed fuel blend.

With a number of exceptions (especially B, F and Se) the above partitioning of elements in entrained flow gasifiers according to their volatile behaviour during gasification is comparable with that reported for coal combustion plants [14,15]. The comparison of the partitioning obtained for the Puertollano IGCC power plant and that of a Spanish PCC power plant co-firing coal and pet-coke [41] show a similar partitioning for the high volatile elements Hg, S, and Cl (70–100% in gas phase), but markedly differences on the partitioning of F, Se, Sn, B, Cd, Sb, As and Zn. The volatile fraction of F, Se, and B is lower for IGCC than for co-combustion, whereas that of As, Sb, Cd and Zn is higher for IGCC than for PCC. The high volatility of As, Sn, Cd and Zn in IGCC is probably caused by the high Cl content of the feed fuel blend of the Puertollano IGCC plant (generally 1300–1700 mg/kg) when compared with the feed fuel of the PCC plant (over 500 mg/kg) and the high fly

ash removal temperatures (265 and 150 °C for IGCC and PCC plant, respectively). If the results of the PCC plant with that of set #4 from IGCC, with similar Cl content in the feed fuel, are compared, the volatile fraction of F, Se, Sn and B is lower than that of PCC even the IGCC fly ash removal temperatures. For this IGCC sample set, the volatile fraction of As and Sb reach the lowest values (<1% volatile), similar to that obtained for PCC. The volatile fractions of Cd and Zn (20% and 10%, respectively) are lower than for other set but still slightly higher than obtained for PCC (5% and <1%, respectively). Therefore, the volatility of As and Sb and in minor degree that of Cd and Zn are controlled by the Cl content of the feed fuel for both, IGCC and PCC plants; reaching very similar partitioning between both power generation technologies. The low volatile proportion of F, Se, Sn and B in IGCC are related to the use of limestone as a fluxing agent in the Puertollano plant, which favours the retention of these elements in fly ash. The high slagging conditions of the Puertollano IGCC facility, account for the opposite distribution of low volatile elements between IGCC (>75% in slag) and PCC (>75% in fly ash) according to the slag/fly ash ratio production.

4. Conclusions

The Partitioning in the Puertollano IGCC plant may be summarised as follows: (a) high volatile elements (70–99% in gas phase): Hg, Cl and S, (b) moderately volatile elements (up to 40% in gas phase and $\geqslant$60% in fly ash): As, Sb, B, F, Cd, Tl, Se, Zn and Sn, (c) elements with high condensation potential: (>90% in fly ash): Pb, Ge, Ga and Bi, (d) elements enriched similarly in fly ash and slag (30–60% in fly ash): Cu, W, (P), Mo, Ni and Na and (e) low volatile elements (>70% in the slag): Cs, Rb, Co, S, K, Cr, V, Nb, Be, Hf, Ta, Fe, U, Ti, Al, Si, Y, Sr, Th, Zr, Mg, Ba, Mn, REEs, Ca and Li. The variability in the volatile behaviour of most of elements in IGCC is controlled by the addition of pet-coke and limestone to the feed fuel blend. Due to the high organic affinity of elements in pet-coke and the high S and Cl content supplied by this fuel, the addition of pet-coke increase the volatile behaviour and the proportion of As, Sb and Tl in the gas phase at removal fly ash temperatures, probably due to a high occurrence of high volatile As–Sn–Tl chloride species. The addition of limestone to the blend in the Puertollano IGCC plant, may change the viscosity of the melt, trapping chlorides and S-bearing species reducing the proportion in gas phase of S, and Cl. Furthermore, the occurrence of B in glass being trapped by the melt at high limestone dosages and in minor degree the potential occurrence of low volatile Ca borates accounts reducing volatility of B.

The main differences among IGCC and PCC plants co-firing coal and pet-coke include: (a) a lower volatility of F, Se and Tl for IGCC plant than PCC due to the high occurrence of condensation processes during IGCC gas cooling and (b) the higher volatility of As, Sb, Sn, Zn and Cd for IGCC than for PCC due to the higher pet-coke proportion used in the gasification blend than in PCC. Furthermore, the slightly higher volatility of Hg in IGCC may be attributable to the relatively low unburned coal particles (char particles may adsorb Hg) of the IGCC raw gas.

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